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Quantitative Analysis of Zirconium Alloys Using Borate Fusion and Wavelength Dispersive X-Ray Fluorescence Spectrometry

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Quantitative Analysis of Zirconium Alloys Using Borate Fusion and Wavelength Dispersive X-Ray Fluorescence Spectrometry

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Abstract

The National Institute of Standards and Technology uses borate fusion, wavelength dispersive X-ray fluorescence spectrometry and synthetic calibration standards for high performance, quantitative analyses of alloys reacted and partially dissolved for fusion into borate beads. Conversion from metal matrix to low Z glass preserves measurement sensitivity. Synthetic calibration standards closely match fused samples, yielding very low uncertainties in results.

This approach was applied to zirconium alloys of $\geq 90\%$ Zr and 17 elements: Al, Co, Cr, Cu, Fe, Hf, Mn, Mo, Nb, Ni, P, Pb, Sn, Ta, Ti, V, and W. To demonstrate capabilities, it was applied to Standard Reference Material (SRM) 360b Zirconium (Sn-Fe-Cr) Alloy, renewal SRM 360c, plus discontinued Zr alloy SRMs: 360, 360a, 1210 through 1215, and 1234 through 1239. Eleven elements exhibit biases $\leq 5\%$ for these SRMs. Additional validation used comparative test methods of inductively coupled plasma (ICP) mass spectrometry, ICP optical emission spectrometry and prompt gamma-ray activation analysis. This WDXRF method gives results of high enough quality to certify the valid elements in conjunction with results from one or more independent methods.

Several phenomena complicate the approach. Normal Zr dissolution using $\text{HNO}_3 + \text{HF}$, forms $\text{Zr}(\text{NO}_3)_4$ in solution and concentrates it on drying. $\text{Zr}(\text{NO}_3)_4$ sublimates at low temperatures, causing uncontrolled loss of Zr as the temperature exceeds $100\text{ }^\circ\text{C}$. Rapidly heated $\text{Zr}(\text{NO}_3)_4$ may explode. Digestion with HF alone works well. High-purity ZrO_2 and LiF were used for matrix matching of calibration standards, requiring determinations of trace elements in the high-purity ZrO_2 .

Introduction

NIST typically uses wavelength dispersive X-ray fluorescence (WDXRF) spectrometry as one test method to quantify elements in alloys. The common approach is to calibrate using alloy reference materials. However, analytical performance of a WDXRF method is often limited by available calibration standards. This is particularly common in the metals industry, because there are many alloy compositions for each of the 10 major base metals. Even when the calibration standards are certified reference materials (CRMs) of the highest caliber, the relative uncertainties of the certified mass fraction values range from $< 1\%$ to $\geq 20\%$. Propagation of high uncertainty into analytical results is unsatisfactory, especially when the analyzed material is intended to be a new CRM. The solution has long been known to be borate fusion [1] with calibration standards prepared from high-purity compounds of established stoichiometry or spectrometric solutions prepared from such compounds.

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When it came time to develop a replacement for SRM 360b, it was desired to include WDXRF in the suite of test methods for quantitative analyses. Commercially pure Zr and alloys of Zr are important to nuclear power generation for electricity and propulsion and to safer burial of spent nuclear fuel. Mass produced alloys include Zr with 2.5 % Nb; Zr with Sn, Fe, Cr and sometimes Ni; and Zr with up to 4.5 % Hf and up to 3 % Nb. The elements Mo, Ta, and W are also added to some alloys. Analyzed impurities in Zr alloys are Ag, Al, B, Bi, Ca, Cd, Cl, Co, Cr, Cu, Fe, Gd, H, Hf, Mg, Mo, N, Na, Nb, Ni, O, P, Pb, Pd, Ru, Sb, Si, Sm, Sn, Ta, Th, Ti, U, V, W, Y, and Zn, which are controlled at maximum allowed mass fractions from 0.5 mg/kg up to 0.2 %, depending on the element and the alloy [2]. ICP mass spectrometry and ICP optical emission spectrometry are the most commonly used test methods, along with inert gas fusion for the gas elements. For these Zr alloy compositions, there are no currently available, solid form SRMs. The only solid form Zr alloy SRMs are the NIST SRM 1210 series and SRM 1234 series, developed beginning about 1960¹ and long out of stock. Attempts to calibrate WDXRF using direct measurements of the SRM 1210 and SRM 1234 series were frustrated by the strong Zr X-ray lines from the alloy matrix. The most intense lines from P, Nb, Mo, and Hf could not be used, which caused the attempt to be abandoned.

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As this paper was undergoing final revisions, it was discovered that a direct, total reflection X-ray fluorescence (TXRF) analysis method had just been published [3]. The method is based on synchrotron radiation with tunable excitation energy and operation at grazing incidence with detection normal to the sample surface. This is specialized equipment not available to normal alloy manufacturers' quality assurance laboratories. Zirconium alloy samples were polished to a mirror finish with measurements representing the near surface region of the metal. Calibrations were created by drying single element solutions on the metal surface and deriving sensitivity factors relative to either Ga K-L_{2,3} at higher excitation energy or Al K-L_{2,3} at lower excitation energy. The method is described as being non-destructive, but it requires significant sample preparation, including the polishing and the deposition of a dried solution containing the Al and Ga internal reference elements on the surfaces of all specimens. Unfortunately, validation data is very limited with no data from CRMs and limited discussion of sources of uncertainty.

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The alternative to direct alloy analysis is to destroy the matrix and to fuse the products in lithium borate flux. Zirconium resists corrosive attack in most organic and mineral acids, strong alkalis, and some molten salts. Solutions of nitric acid (HNO₃), sulfuric acid (H₂SO₄), and hydrochloric acid (HCl) with impurities of ferric, cupric and nitrate ions generally result in corrosion rates < 0.13 mm/year, even at temperatures above boiling [3]. A tightly adherent oxide film protects the metal-oxide interface to provide corrosion resistance. For destructive analysis, Zr and its alloys can be reacted with HNO₃ containing HF. The metal can be quantitatively dissolved in aqueous solution for analysis [4], but that is not necessary for borate fusion.

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For borate fusion, the reacted metal, either dissolved or in slurry, must be taken to dryness prior to fusion at high temperatures. When HNO₃ is present, the Zr predominantly forms Zr(NO₃)₄, which sublimates at 95 °C. The result is a plume of white vapor indicating significant loss of Zr and a potential inhalation hazard [5]. In addition, nitrate compounds present an explosion hazard, if

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¹ There are a few commercially produced CRMs, which were not available to the NIST researchers at the time of project implementation.

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3 heated too rapidly. Therefore, HNO_3 must be avoided. The alternative is reaction with
4 concentrated HF. Although the potential for serious injury from HF [6] is a concern, it is not as
5 potentially hazardous as an explosion and possible fire. Personal protective equipment,
6 engineering controls and training can mitigate the hazards of HF. Plus, it may be possible to reduce
7 the amount of HF, which the authors did not investigate.
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10 The method presented herein demonstrates a quantitative analysis process based on borate fusion
11 sample preparation and WDXRF measurements. The level of detail provided is based on the
12 assumption the reader has experience with both borate fusion and WDXRF. Calibration standards
13 are prepared from single element CRM solutions to impart metrological traceability to the
14 International System of Units (SI). Although the dilution factor of 16 is relatively high, most
15 elements were quantified, including those with lines swamped by Zr lines in direct alloy analysis.
16 The elements Cd, Mg and U were too dilute in the alloys and could not be detected in fused beads.
17 A distinct advantage of the dilution is the reduction of specimen Zr content to about 6 %, which
18 substantially reduced the well-known interferences due to overlaps of Zr peaks on peaks from P,
19 Nb, Mo, Hf, and Pb.
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22 **Equipment**

23 The following equipment was used in this work.

24 Balances: A model MSA225S balance (Sartorius) was used for weighing samples and ingredients
25 for calibrants. A model LP1200S balance (Sartorius) was used for weighing flux quantities for
26 fused specimens.
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28 Oven: Heat treatments of high-purity compounds were done in a Lindberg/Blue M model
29 BF51842PBFMC box furnace.
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31 Borate Bead Machine: Model K1 Prime (Katanax) electrically heated fusion machine with
32 crucibles and casting dishes of 95 % Pt/5 % Au alloy.

33 WDXRF Spectrometer: Model Zetium Ultimate WDXRF spectrometer (Malvern Panalytical).
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36 **Reagents**

37 The following ingredients were used in this work.

- 38 ▪ Purified H_2O ($< 20 \mu\text{S}$) was used to create the LiI solution and to dilute SRM spectrometric
39 solutions prior to weighing.
- 40 ▪ The non-wetting solution was prepared from LiI, 99.995 % pure on metals basis (Alfa Aesar),
41 dissolved in purified H_2O to make a 25 % by mass solution.
- 42 ▪ Fused bead specimens have flux composition 67 % LiBO_2 /33 % $\text{Li}_2\text{B}_4\text{O}_7$ created using pre-
43 fused, high-purity, 50/50 $\text{Li}_2\text{B}_4\text{O}_7$ / LiBO_2 (Spex Certiprep) and high-purity LiBO_2 (VHG
44 Labs).
- 45 ▪ Zirconium oxide, 99.978 % pure on metals basis (Alfa Aesar), was heat treated at 1150 °C for
46 2 h to ensure stoichiometry and freedom from adsorbed contaminants [7, 8].
- 47 ▪ NIST primary zirconium metal, lot NP-Zr-1, was used as an alternative to ZrO_2 . This metal
48 was used to create SRM 3169 Zirconium Standard Solution [9] and was assayed by multiple
49 methods.
- 50 ▪ Hydrofluoric acid, 48 % ACS reagent grade (GFS Chemicals), was used to digest alloy
51 samples.
- 52 ▪ Lithium fluoride, 99.999+ % pure (Materials Research Corp.), was used to matrix match the
53 fluorine contents of synthetic calibration standards to the digested and fused alloy samples.
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- NIST SRM 3100 series solutions were used as sources for elements in synthetic, fused bead calibration standards: 3101a Aluminum (lot 140903), 3112a Chromium (lot 170630), 3113 Cobalt (lot 000630), 3114 Copper (lot 120618), 3122 Hafnium (lot 151120), 3126a Iron (lot 140812), 3128 Lead (lot 101026), 3132 Manganese (lot 050429), 3134 Molybdenum (lot 130418), 3136 Nickel (lot 120619), 3137 Niobium (lot 120629), 3139a Phosphorus (lot 060717), 3161a Tin (lot 140917), 3155 Tantalum (lot 110715), 3162a Titanium (lot 130925), 3163 Tungsten (lot 140606), and 3165 Vanadium (lot 160906).

Borate Fusion Process

All alloys were prepared as lathe turnings (commonly called chips) 0.5 mm to 2 mm wide and 2 mm to 10 mm long. Chips are easily obtained with minimal risk of contamination by using hard, tool steel cutting tools. Use caution and cut slowly to avoid overheating the chips of Zr, which can burn in air. In 50 mL fluorinated ethylene propylene (FEP) beakers and using a five-place analytical balance, 0.50xxx g of alloy chips was weighed into 10 mL H₂O. After the beaker was transferred to a fume hood, 1 mL concentrated HF was added dropwise until a reaction began. After the first few drops, HF addition was done one or two drops at a time to minimize the rate of reaction, because every bubble that bursts sprays droplets that can easily leave the beaker. It took ≈ 20 min to add the HF, allowing the reaction to subside after each addition. The beakers were kept covered as much as possible, using Teflon watch glasses. When the reaction was complete, the product was a clear solution with a small quantity of fine, black particles, some floating and some on the bottom of the beaker. The beaker walls and watch glass were rinsed into the beaker with 1 mL to 2 mL of H₂O. During the digestion, a Pt/Au crucible and casting dish were cleaned in dilute HCl (1:4 in H₂O) in an ultrasonic bath, blown dry with compressed air, and weighed empty.

The beaker contents were transferred in small aliquots to the Pt crucible and taken to dryness in an oven at 107 °C. The lack of observable free water was taken as dry enough to add the next aliquot. Aliquots of < 5 mL kept the liquid level in the crucible below the height at which molten glass laps the surface during rocking by the fusion machine. The volume of rinse water was minimized to avoid lengthening the drying process, which took most of a day. That's no problem, because multiple samples can be processed simultaneously. The dried reaction products formed a translucent, solid layer in the bottom of the crucible. Lithium borate flux was added by weight, using a top loader balance (1 mg resolution), and the crucible contents were ready for fusion. Flux quantities were recorded but not used in calculations. The amount of flux added at this point was ≈ 0.1 g less than the amount calculated to make 8.0 g total glass. The quantities and proportion of the two fluxes were optimized to enhance Zr solubility with a dilution factor of 16. Using the Claisse Calculator [10], the bead oxygen/metal (O/M) atomic index is 1.114, which is near the optimum value of 1.15 for creating a vitreous bead.

Fusion with the Katanax K1 Prime required a multiple-step program with steps 1, 2, 3, 4, 8, and 9 done by the borate fusion machine. The full stepwise procedure is as follows:

Step 1: Crucible heated to T = 200 °C, hold 3 min; Step 2: Heat to T = 600 °C, hold 2 min; Step 3: Heat to T = 1000 °C, hold 15 min, no mixing; Step 4: Hold T = 1000 °C, hold 19 min, mix by rocking; Step 5: Cool to room T, break glass, return to crucible; Step 6: Repeat Steps 1 through 4, then cool to room T; Step 7: Add 4 drops LiI solution; Step 8: Heat crucible to

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3 T = 1030 °C and dish to T ≥ 900 °C, hold 2 min, pour into dish; Step 9: Cool unassisted 25 s, then
4 forced air until dish T < 100 °C, return crucible to upright position.
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7 Steps 1 and 2 remove H₂O from the crucible contents and promote full oxidation. These steps are
8 not needed for the repeat of the first four steps, but they don't hurt either. It is important for the
9 first fusion step (Step 3) to have no mixing to promote dissolution of MO₂ oxides. In Step 5, the
10 glass usually cracked on cooling. It was removed onto glassine weighing paper and returned to
11 the crucible to promote mixing. The total fusion time was 68 min. When the glass was cooled to
12 room temperature the second time, the crucible was weighed, and a quantity of flux was added to
13 get a total glass weight of 8.0x g. Steps 8 and 9 were run in a separate bead machine program. In
14 Step 8, the temperature was ramped to 1030 °C as rapidly as possible. In Step 9, cooling the dish
15 below 100 °C prevents dish temperature from rising to > 300 °C, after the fan stops. It is advisable
16 to keep the crucible in its pour position until the glass has solidified completely to avoid
17 crystallization caused by motion of the vitreous, liquid glass. When the crucible and dish reached
18 room temperature in Step 9, they were weighed with their contents, using the analytical balance.
19 The total amount of glass formed was calculated. With 32 mm casting dishes and a total glass
20 weight of 8.0 g, the lowest dilution for Zr metal that yielded good beads was determined to be a
21 factor of 16. Because HF is typically contaminated with Si from equipment employed in its
22 manufacture, reaction with HF prevents analysis of Si by imparting contamination amounting to
23 estimated levels of 20 mg/kg to 50 mg/kg in the beads.
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27 Alloy samples for this project were duplicate samples from each of six bottles (12 samples total)
28 of SRM 360c Zirconium (Sn-Fe-Cr) Alloy, four samples of SRM 360b for quality assurance, and
29 one sample of each Zr alloy SRM: 360, 360a, 1210, 1211, 1212a, 1213, 1214, 1215, 1234, 1235,
30 1236, 1237, 1238, and 1239 (certificates are available from [https://www-
31 s.nist.gov/srmors/view_detail.cfm?srm=360B](https://www-s.nist.gov/srmors/view_detail.cfm?srm=360B) and in the Archive collection at [https://www-
32 s.nist.gov/srmors/certArchive.cfm/](https://www-s.nist.gov/srmors/certArchive.cfm/)). SRMs with 12xx numbers are solid form from which chips
33 were prepared during their original certification projects. For better productivity, two crucibles
34 and two casting dishes were used during production of the 30 fused beads and the fused, synthetic
35 calibration standards.
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39 **Synthetic Calibration Standards**

40 Calibration standards were designed to cover the mass fraction ranges for the 17 alloy and
41 contaminant elements from blank level to the highest mass fraction in a fused bead. Table 1 shows
42 the compositions of the eight calibration standards. Zirconium was calibrated in a narrow range
43 from 5.90 % to 6.25 % in the beads. Primary calibrants for the alloy and contaminant elements
44 were SRM 3100 series single element solutions, and the source of Zr was high-purity ZrO₂. Target
45 mass fractions were calculated from the certified and information values, plus some unpublished
46 analysis results, for the suite of SRMs listed in the previous section. To avoid weighing low
47 solution masses that carry high relative uncertainty due to the limitations of the balance, most SRM
48 solutions were diluted by a factor from 2 to 17, using lab pure H₂O.
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51 To prepare each calibrant, roughly half the required flux was weighed into a clean, weighed Pt/Au
52 crucible. Each solution aliquot was weighed by dropwise addition into the flux in the crucible on
53 an analytical balance. To make it easier to get stable readings of mass for the aqueous solutions,
54 a cover was placed onto the crucible after the aliquot was added. After weighing, each aliquot of
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3 solution was taken to dryness, and the process was repeated until all elements were in the crucible.
4 ZrO₂ was added by weight, followed by 0.50 g high-purity LiF to match the amount of F in the
5 alloy samples from HF digestion. The quantity of LiF was arrived at by trial and error, making Zr
6 and F containing beads until F count rates were close to count rates from selected fused alloy
7 samples. This process must only be done one time during method implementation, and it takes
8 only a few tries to get a good estimate of the necessary amount of LiF. During fusion, 0.50 g LiF
9 converts to 0.74 g of (Li₂O + F). LiF required no pretreatment, because it was for matrix matching
10 only. Last, the remaining flux was weighed on top of the dried ingredients. Again, the amount of
11 flux for fusion was short about 0.1 g, which was added just prior to running the program for bead
12 casting to get all total glass masses in the range of 8.00 g to 8.05 g. The same fusion process was
13 used as for the reacted metal samples.
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17 One additional calibration standard was prepared from NIST primary Zr metal used to create
18 SRM 3169 Zirconium Standard Solution. This batch of Zr metal was carefully assayed to serve
19 as a primary reference for amount of Zr and has known values for trace levels of Al, V, Cr, Mn,
20 Fe, Ni, Cu, Hf, Ta, and Pb.
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22 **Measurements**

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24 The WDXRF measurement program consisted of 45 sequential measurements of peak and
25 background count rates shown in Table 2. Measurements made under vacuum include all
26 analytes, plus the Rh Compton peak from the X-ray tube, the Pt L₂-M₄ line to monitor Pt uptake
27 in beads, and the I L₂-M₄ line for a line overlap correction of the I L₃-N_{4,5} line on the Ti K-L_{2,3}
28 line. Peak measurement times were chosen to obtain counting uncertainty estimates ≤ 0.5 %
29 relative. Background measurement times were less than or equal to peak times. Special choices
30 of lines are the Hf L₂-M₄ and Mo L₂-M₄ lines to avoid stronger overlaps from Zr lines and use of
31 the Al filter for Nb and Pb to reduce the Zr overlaps.
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34 All measurements were made in order from high energy to low energy. Where a single background
35 location was measured for an element, a background slope factor was used to get a better estimate
36 of the true count rate at the peak angle. Where four background locations were measured, the
37 background calculation factors were fixed to set the same background curve shape for all samples.
38 The viewed area of the samples was defined by a 29 mm diameter mask. All fused samples and
39 synthetic calibrants were measured in a single batch with samples done in random order, followed
40 by calibrants.
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43 As shown in Table 2, four background measurements were obtained for both P and Mo to enable
44 fitting of curved background shapes for better background estimates. See Figure 1 for phosphorus
45 as an example. Figure 1 shows the relative intensities of the Zr L₃-M_{4,5} lines peak and the P K-L_{2,3}
46 peak in a fused bead made from SRM 1215. The P peak comes from approximately 13 mg/kg in
47 the bead, and the Zr peak comes from approximately 6 % Zr. As shown in Table 1, the amount of
48 Zr in all beads is in the narrow range from 5.9 % to 6.25 %, which means the background shape
49 beneath the P peak is constant, and the curve fitted to the four background measurements is
50 expected to be equally reliable for every specimen.
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Calibrations

All elements used the linear calibration model in Equation 1, where for element i , x_i = mass fraction, b_{0i} = intercept (mass fraction units), b_{1i} = slope (mass fraction/count rate units), and R_i = count rate (gross or net). No interelement absorption corrections were applied. For the Cr, Fe, Sn, and Ta regressions, weighting with the weighting factor set equal to the inverse mass fraction was used to force the calculated curves to fit better the lower mass fraction calibration points. Weighting was needed for these elements due to the heteroscedastic nature of X-ray data and the very wide ranges of mass fractions among the calibration standards. In a very wide range set of points without this weighting, the highest mass fraction points will control the regression fit of the calibration model, because those points represent much lower relative differences between known and calculated mass fractions than can be obtained for the very low mass fraction points. Other elements did not need weighting, because their calibration points were mostly low mass fractions, which closely covered the ranges of mass fractions found in the beads. The Rh Compton peak count rate was used as the ratio rate for Ta, i.e. substituting R_{Ta}/R_{Rh} for R_{Ta} , because it significantly improved the goodness of fit as evaluated using the root-mean-square differences between known and found mass fractions for the calibration standards. For Ti, the line overlap term l_{Ti} was added to the right side of Eq. 1 to correct for the overlap of I L₃-M_{4,5} on Ti K-L_{2,3}. The overlap factor for I on Ti was determined in a separate experiment, using fused portland cement samples. Line overlap factors were also included for Ta on Cu, Cu on Ta, and Ta on W, all calculated as functions of the measured count rates.

$$x_i = b_{0i} + b_{1i}R_i \quad (1)$$

Determinations were completed by converting the found mass fractions in the fused beads to the original sample basis, using Equation 2, where X_i = mass fraction in the alloy, m_g = total mass of borate glass created by fusion, and m_s = mass of sample.

$$X_i = x_i m_g / m_s \quad (2)$$

ZrO₂ Impurities: Because the ZrO₂ used to matrix match the synthetic calibrant beads is known to contain traces of several key elements, the calibrations were evaluated for effects of known or potential impurities causing high biases of the intercepts of curves. The certificate of analysis of the ZrO₂ [7] lists estimates obtained using “Inductively Coupled Plasma Analysis”: < 20 mg/kg Al, < 25 mg/kg Cr, < 25 mg/kg Cu, < 20 mg/kg Fe, < 25 mg/kg Hf, 20 mg/kg Na, < 25 mg/kg Pb, 165 mg/kg Si, and < 25 mg/kg Ti. Other elements of interest were listed as not detected, including Co, Mn, Mo, Nb, Ni, P, Sn, Ta, and W. Synthetic calibrant beads intended to be blank for each element were compared to the bead prepared from NP-Zr-1 metal. In the synthetic calibrants, the elements Al, Cr, Fe, Hf, Ni, and Pb were observed to give higher net count rates. For Al, Cr, Hf, Ni, and Pb, those blank beads were removed from the calibration fit to minimize bias to the intercept. For Fe, an estimate of the amount in the ZrO₂ was obtained, and corrections were applied as follows.

Preliminary results from this new method for Fe in the alloy SRMs showed a low bias of ≈ 30 mg/kg on the original sample basis, which suggested there may be tramp Fe in one or more ingredients of the beads. This amount of Fe would be equivalent to about an extra 2 mg/kg Fe in the synthetic calibration standards. Comparisons of beads made with ZrO₂ with and without LiF

showed no detectable Fe due to the LiF. Using SRM 3126a, a standard additions calibration was created to determine Fe in blank beads made from flux, ZrO₂ and LiF, but it failed to provide quantitative results, due to poor reproducibility among the spiked samples. The bead prepared from the NP-Zr-1 Zr metal was used as a single calibration standard to give a mean value of 2.5 mg/kg Fe in four beads made from ZrO₂. That amount is equivalent to 31 mg/kg Fe in the ZrO₂, which matches the bias observed in the preliminary calibration. Table 1 shows the compositions of the eight calibration standards, after adjustment of the Fe values for this tramp Fe.

Results and Discussion

Performance evaluations were made by 1) comparing found and known values for the 14 discontinued SRMs; 2) using SRM 360b for quality assurance, and 3) comparisons of WDXRF results for candidate SRM 360c to results from independent test methods.

Zr Alloy SRMs: With the range of Zr alloy SRM compositions analyzed, the correlations between found and certified mass fractions are shown graphically in Figure 2. The slope of each correlation line (black curve in each graph) indicates the average bias at higher mass fractions, and the intercept represents blank bias in the calibration curve. The red line is the ideal case where there are no biases with slope = 1 and intercept = 0. Graphs for Cr, Fe, Mn, Co, Ni, Cu, Sn, Hf, and Ta show excellent performance with < 5 % relative slope bias and negligible intercept bias between the two lines. The performance for Fe was improved by including the 31 mg/kg Fe found in the ZrO₂, where a 33 mg/kg low intercept bias was reduced to 0.33 mg/kg. The intercept for Sn was set equal to zero, because there are no certified Sn values < 0.95 %. Graphs for Al, Ti, Nb, Ta, and Pb show biases in either slope or intercept. However, apparent biases for Ta and Pb are not important in light of the agreements among results for SRM 360c shown in Table 4 and for SRM 1237 shown in Table 5. Graphs for P and V show poor results, because the known values came from documented spark optical emission spectrometry test results from the old SRM development records. It is likely those old results are of poor quality. For Mo, the certified value for SRM 1211 and the information value for SRM 1239 appear to be significantly biased with found results substantially greater than assigned values. Without those values, the performance is markedly better. The information values used in these comparisons for P, V, and Mo were obtained from archived records, have little or no supporting documentation, and have not been confirmed by a second method.

SRM 360b: As the only Zr alloy SRM currently for sale, SRM 360b represents the best choice for a quality assurance material. It has seven certified values, five reference values and six information values to compare to found results. Table 3 contains the compiled WDXRF results for SRM 360b and the individual uncertainty components from the test method. Figure 3 shows how the mean found results for SRM 360b compare to the certificate values with excellent agreement, except Fe where the found results are clearly lower than the certificate value. Sample 4 was not used for Fe, because the bead had several small spots on its surfaces in which microXRF measurements found unusually high in Fe content. Results shown as less than (<) values are defined as limits of detection, where $L_D \approx 3s$. Certified and reference values have expanded uncertainty estimates, $U_{k=2}$, and information values are all 'less than' values that indicate NIST believes the true values are less than the given number. Individual uncertainty components are repeatability standard deviation, s ; standard uncertainty of calibration model fit to the data, u_m for p calibration standards; standard uncertainty of the primary calibration standard, u_s ; and standard uncertainty of weighing,

u_b for balance calibration and linearity. The combined standard uncertainty is u_c , calculated using Equation 3, where the balance calibration term is multiplied by two for the two masses used and divided by three under the assumption of a uniform uncertainty distribution.

$$u_c = \sqrt{s^2/(n-1) + u_m^2/p + u_s^2 + 2u_b^2/3} \quad (3)$$

In the same way as for SRM 360c in Table 4, estimates of L_D replace mean results values where appropriate. All L_D values are consistent with certificate information values. Only Pb has a problem where the found mean result is greater than the information value, which is consistent with the 8.8 mg/kg high bias (intercept) shown in Fig. 2.

Bias values, Δ , are shown as absolute values of the differences between found and SRM values. Bias detection limits, Δ_D , were calculated according to Equation 4 taken from ISO Guide 33 [11], where $k = 2$ is the coverage factor for approximately 95 % confidence, u_{Found} is the combined standard uncertainty of the found result, and u_{SRM} is the combined standard uncertainty of the certified or reference value. For Fe, there is a detected low bias ≥ 94 mg/kg. For Ni, the negative bias of 6 mg/kg, shown in Fig. 1a, accounts for most of the difference between the found and certified values.

$$\Delta_D = k\sqrt{u_{\text{Found}}^2 + u_{\text{SRM}}^2} \quad (4)$$

Comparative Test Methods: In the development project for SRM 360c, NIST applied three test methods in addition to borate fusion WDXRF: inductively coupled plasma mass spectrometry (ICPMS), inductively coupled plasma optical emission spectrometry (ICPOES) and prompt gamma-ray activation analysis (PGAA). Likewise, ATI Specialty Components and Alloys performed determinations using ICPMS and ICPOES. Results were reported for SRM 360c and for SRM 360b as a quality assurance material, plus NIST ICPMS was used on SRM 1237 Zircaloy D, which is certified for Hf and has information values for numerous other elements. Table 4 contains results and uncertainty estimate values from all four methods from the two laboratories. Where there are two or more test methods for an element, an overall mean and standard deviation are shown to demonstrate the extent of agreement. Agreement is good for most elements with the relative standard deviations (%rsd) as high as 7.6 %. Thus, there are two or more independent test methods for the elements P, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Nb, Sn, Ta, W, and Pb. Poor agreement is shown for P between WDXRF at 24.7 mg/kg and the ICP method results, which agree at 87.6 mg/kg. WDXRF does not have the sensitivity to quantitatively determine Al, Ti, Mn, Cu, and Mo in SRM 360c, because the dilution factor is 16. However, the listed L_D values are in general agreement with the results from other methods.

For SRM 1237, Table 5 contains a comparison of WDXRF and NIST ICPMS results that gives more information on the accuracy of the two methods. The information is limited, because just one sample of SRM 1237 was analyzed by WDXRF, preventing the presentation of any uncertainty estimates, and because most of the certificate values are information values. Both test methods gave good results for Mn, Co, Cu, Ta, and W. Both methods agree well for Nb, and the results appear to invalidate that listed information value. ICPMS results were superior to WDXRF

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3 results for Hf, as discussed below. Both methods gave biased results for P with the mean of the
4 two methods being similar to the information value. Results from both methods for Ti, V and Ni
5 agree well enough to appear to invalidate those listed information values.
6

7
8 Biased Results for Hafnium: With dilution of the alloys by 16 in borate beads, it becomes possible
9 to quantitatively determine Hf in the presence of high Zr. The results for Hf in specimens of
10 SRM 360c are shown in Table 4 with a mean of 30.6 mg/kg. This is a corrected value based on
11 the following discussion. The original WDXRF result for Hf was 20.6 mg/kg, which is low
12 compared to the results from other methods shown in Table 4. The original, low Hf result for
13 SRM 360c is also at odds with the good WDXRF result obtained for SRM 360b. One hypothesis
14 is that composition differences between SRM 360b and SRM 360c cause the WDXRF bias.
15

16
17 For all SRMs in Fig. 2, except four, the Hf results agree with the certified or information values as
18 shown by their proximity to the red line. Low Hf results for SRMs 1236, 1237, 1238, and 1239
19 indicate there is a bias for Hf under certain conditions. The blue curve in Fig. 2 shows the bias in
20 results for these four SRMs is -9.2 mg/kg at the intercept and 8.6 % low at higher mass fractions.
21 One hypothesis is these four SRMs have the sum of Nb + Ta > 600 mg/kg. For SRM 1237, the
22 WDXRF result for Hf in Table 5 is low compared to the ICPMS result, with Nb + Ta = 295 mg/kg
23 and Mo = 762 mg/kg. This hypothesis does not fully explain why the original WDXRF Hf result
24 for SRM 360c is biased low, because it has Nb + Ta = 300 mg/kg and low Mo. Because the
25 measured X-ray lines from these elements are in a narrow range of Bragg angles, it was concluded
26 that a more in-depth study of matrix interferences is needed to try to improve the Hf calibration.
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30 Equation 5 is a correction calculation based on a simple normalization for the differences between
31 the black line and the blue line for Hf without attempting to account for effects of other elements,
32 where S = slope, I = intercept, $orig$ = original curve (black line in Fig. 2) with all Hf values, and
33 $bias$ = curve for SRMs with biased Hf results (blue line in Fig. 2). To a first approximation, the
34 uncertainty of the correction is assumed to equal the uncertainty of the calibration model, u_m , for
35 Hf. Therefore, the uncertainty for the corrected Hf result has been increased by substituting $2u_m$
36 in the calculations of U .
37

$$38 \quad [Hf]_{cor} = ([Hf]_{orig} - I_{bias})(S_{orig}/S_{bias}) + I_{orig} \quad (5)$$

39
40
41
42 If corrected for the bias shown by the blue line in Fig. 2, the mean WDXRF Hf result for SRM 360c
43 becomes 30.6 mg/kg, which agrees well with the NIST ICPMS result of 33.36 mg/kg and the other
44 results listed in Table 4. The corrected WDXRF Hf result for SRM 1237 is 26.9 mg/kg, which
45 agrees better with the NIST ICPMS result of 32.54 mg/kg Hf.
46

47 **Conclusions**

48
49 The new borate fusion sample preparation approach uses concentrated HF to react and mostly
50 dissolve Zr and Zr alloys, allowing them to be fused with a moderate dilution factor of 16. To
51 improve on this new borate fusion WDXRF test method, it is necessary either to obtain a source
52 of Zr having better purity for Fe and other elements or to assay the ZrO₂ for those elements.
53 Relatively unbiased results for those elements were possible only because of the availability of the
54 NP-Zr-1 assayed Zr metal.
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The majority of WDXRF results are accurate across the suite of SRMs in the 1200 series, SRM 360, and SRM 360a. The one unresolved difficulty is for Hf, for which there is not good explanation and more work is needed. Using the data in this work, a correction was applied, based on the curves for Hf in Fig. 2. That would not be possible in a lab that does not have the discontinued 12xx series Zr alloy SRMs. To find and correct the source of the calibration bias would require additional calibration standards to enable calculation and testing of correction factors for possible line overlaps and absorption effects. Of course, it is possible the original values for Hf in some of those SRMs were biased all along.

The test method demonstrated herein is relatively time consuming and may not be attractive to laboratories requiring high sample throughput. In addition, the use of synthetic calibration standards requires the lab to have some knowledge of the compositions of their samples before implementing the method. This should not be a serious problem, because Zr alloys have manufacturing specifications for element mass fractions and all elements present at milligram per kilogram levels can be calibrated over a standardized range up to several hundred mg/kg. The authors developed the method as an independent approach to be used in reference material development. Therefore, the method should be helpful to labs that must develop in-house reference materials [12].

Disclaimer

Certain commercial equipment, instruments or materials are identified in this document to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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12 **Keywords**

13 borate fusion, elemental analysis, quantification, Standard Reference Material, X-ray fluorescence
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Table 1. Synthetic Calibration Standards for Zirconium Alloy Fused Beads

	SYN-1	SYN-2	SYN-4	SYN-6	SYN-7	SYN-8	SYN-9	SYN-10	NP-Zr	Unit
Al	□	5.69	9.35	□	□	27.91	22.50	36.39	14	mg/kg
P	43.81	□	18.32	□	□	□	8.972	30.34	-	mg/kg
Ti	□	3.09	5.80	□	□	□	11.99	10.62	6	mg/kg
V	3.40	9.47	6.14	□	□	□	□	□	0.023	mg/kg
Cr	116.88	□	71.33	85.13	108.67	92.10	46.42	50.45	0.12	mg/kg
Mn	□	8.22	10.26	□	□	□	18.95	41.62	0.019	mg/kg
Fe	107.91	172.98	79.54	106.01	105.18	73.51	1.66	1.66	2.7	mg/kg
Co	10.83	□	5.60	□	□	7.31	2.61	4.09	-	mg/kg
Ni	□	5.384	24.49	□	□	□	58.98	42.24	0.048	mg/kg
Cu	2.351	16.20	7.64	□	□	□	□	21.15	0.038	mg/kg
Zr	6.2479	6.1949	6.1807	5.9323	6.1802	6.1633	6.1288	6.1391	6.18	%
Nb	38.52	□	6.61	4.27	5.43	3.40	3.55	14.48	-	mg/kg
Mo	□	5.22	11.65	□	□	□	14.54	22.09	-	mg/kg
Sn	0.05948	0.13058	0.07514	0.11975	0.12475	0.10076	0.00404	0.03030	-	%
Hf	26.84	□	10.61	□	□	□	6.00	44.26	4.0	mg/kg
Ta	□	24.44	39.21	11.64	12.13	9.50	42.68	63.38	0.0049	mg/kg
W	5.34	37.78	28.88	□	□	□	□	19.15	-	mg/kg
Pb	16.14	□	9.63	□	□	□	4.11	23.32	0.013	mg/kg

Entries of □ indicate element not added. Entries of - indicate element not analyzed in NP-Zr.

Table 2. Measurement Conditions for Fused Beads

	Line	kV, mA	Filter	Crystal	Collimator	Detector	Peak Time (s)	Backgrounds
Rh	K-L _{2,3}	60, 66		LiF220	100 μm	SC	30	
Nb	K-L _{2,3}	60, 66	Al	LiF220	100 μm	SC	40	-1
Zr	K-L _{2,3}	60, 66	Brass	LiF220	100 μm	SC	2	
Pt	L ₂ -M ₄	60, 66		PX10	300 μm	SP	60	-1
Pb	L ₃ -M _{4,5}	60, 66	Al	PX10	300 μm	SP	80	1
Hf	L ₂ -M ₄	60, 66		PX10	300 μm	SP+FP	200	-1
W	L ₃ -M _{4,5}	60, 66		PX10	300 μm	SP+FP	100	-1
Ta	L ₃ -M _{4,5}	60, 66		PX10	300 μm	SP+FP	50	-1
Cu	K-L _{2,3}	60, 66		PX10	300 μm	SP+FP	50	-1
Ni	K-L _{2,3}	60, 66		PX10	300 μm	SP+FP	50	1
Co	K-L _{2,3}	60, 66		PX10	300 μm	SP+FP	110	1
Fe	K-L _{2,3}	60, 66		PX10	300 μm	SP+FP	10	1
Mn	K-L _{2,3}	60, 66		PX10	300 μm	FP	70	1
Cr	K-L _{2,3}	50, 80		PX10	300 μm	FP	50	1
V	K-L _{2,3}	50, 80		PX10	300 μm	FP	140	1
Ti	K-L _{2,3}	40, 100		PX10	300 μm	FP	120	1
I	L ₂ -M ₄	40, 100		PX10	300 μm	FP	130	1
Sn	L ₃ -M _{4,5}	25, 160		PX10	300 μm	FP	30	-1
Mo	L ₂ -M ₄	25, 160		Ge111	100 μm	FP	300	-2, +2
P	K-L _{2,3}	25, 160		Ge111	300 μm	FP	170	-2, +2
Al	K-L _{2,3}	25, 160		PE	700 μm	FP	130	-1

Al = 750 μm, Brass = 100 μm

PX10 = synthetic multilayer, PE = pentaerythritol

SC = scintillation, SP = sealed Xe proportional, FP = flow P10 proportional

Backgrounds: + and - indicate number of measurements on each side of peak

Table 3. Compiled XRF Results and Bias Test for SRM 360b

Sample	Al (mg/kg)	P (mg/kg)	Ti (mg/kg)	V (mg/kg)	Cr (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	Co (mg/kg)	Ni (mg/kg)
1	58.2				1025		2036		12.9
2	36.5				1021		2037		18.6
3	43.3				1016		2058		14.8
4	46.2				1098		2200 ^(a)		15.6
Mean	46.0	< 10	< 20	< 5	1040	< 20	2044	< 8	15.5
<i>s</i>	9.1				39		12		2.9
<i>n</i>	4	4	4	4	4	4	3	4	4
<i>u_m</i>	1.2				13		34		0.27
<i>p</i>	9	9	9	8	9	5	9	9	5
<i>u_s</i>	0.042				1.1		2.5		0.020
<i>u_b</i>	0.014				0.31		0.61		0.0046
<i>u_c</i>	5.3				23		15		1.7
<i>U_{k=2}</i>	11				46		29		3.3
Certificate	57	8.7	15.5	< 30	1043	9.2	2138	0.97	22.5
<i>U</i>	11				18		42		4.4
Δ	11				3.0		94		7.0
Δ_D	15				49		51		5.5
Bias Detected	No	No	No	No	No	No	Yes	No	Yes

Sample	Cu (mg/kg)	Zr (%)	Nb (mg/kg)	Mo (mg/kg)	Sn (%)	Hf (mg/kg)	Ta (mg/kg)	W (mg/kg)	Pb (mg/kg)
1	15.6	97.45	6.9	56	1.5224	78.7	5.7		7.6
2	13.3	98.08	8.5	66	1.5281	72.3	7.8		6.7
3	11.8	97.91	5.5	15	1.5190	72.9	8.3		7.3
4	14.9	98.09	24.7	42	1.5314	87.0	8.0		10.5
Mean	13.9	97.88	< 30	< 100	1.5252	77.7	7.4	< 10	8.0
<i>s</i>	1.7	0.30			0.0056	6.8	1.2		1.7
<i>n</i>	4	4	4	4	4	4	4	4	4
<i>u_m</i>	0.30	1.6			0.015	3.4	0.12		0.18
<i>p</i>	9	11	9	8	9	5	10	9	9
<i>u_s</i>	0.017	0.20			0.0019	0.082	0.0080		0.0056
<i>u_b</i>	0.0042	0.029			0.00046	0.023	0.0022		0.0024
<i>u_c</i>	0.99	0.56			0.0063	4.2	0.70		0.99
<i>U_{k=2}</i>	2.0	1.1			0.013	8.4	1.4		2.0
Certificate	12.5	98.43	< 50	< 25	1.555	78.5	< 100	< 50	< 5
<i>U</i>	1.7	^(b)			0.057	2.3			
Δ	1.4	0.54			0.030	0.80			
Δ_D	2.6	1.1			0.058	8.7			
Bias Detected	No	No	No	No	No	No	No	No	Yes

^(a) Value from bead contaminated with spots rich in Fe from unknown source. Value not used.

^(b) Zr Certificate value calculated by difference of listed values from 100 %.

Table 4. Comparison of WDXRF, ICPMS, ICPOES, and PGAA Results for Candidate SRM 360c

Element:	Al	P	Ti	V	Cr	Mn	Fe	Co	Ni
	(mg/kg)								
Method									
WDXRF Mean	< 30	24.7	< 20	18.4	1530	< 20	1553	5.54	14.0
<i>U</i>		1.5		1.9	15		20	0.85	2.2
NIST ICPMS Mean		85.0	13.43	19.92		6.613		5.102	19.71
<i>U</i>		1.2	0.52	0.97		0.096		0.066	0.28
NIST ICPOES Mean			< 15		1523	< 15	1636		17.2
<i>U</i>					17		21		1.3
NIST PGAA Mean					1557		1631		19.37
<i>U</i>					20		20		0.90
ATI ICPOES Mean		90.1	11.7	20.0	1579	7.80	1581		19.21
<i>U</i>		4.2	1.0	3.0	48	0.50	50		0.86
ATI ICPMS Mean	21.45								16.20
<i>U</i>	0.82								0.68
Overall Mean	21.45	67	12.6	19.44	1547	7.21	1600	5.32	17.6
<i>s</i>		36	1.2	0.90	26	0.84	40	0.31	2.3
%rsd		55	9.5	4.6	1.7	12	2.5	5.8	13
Element:	Cu	Nb	Mo	Sn	Hf	Ta	W	Pb	
	(mg/kg)	(mg/kg)	(mg/kg)	(%)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	
Method									
WDXRF Mean	< 8	106.5	< 100	1.959	30.6	193.7	24.7	8.7	
<i>U</i>		4.5		0.017	2.3	3.1	1.6	1.4	
NIST ICPMS Mean	5.299	103.7			33.36	201.1	22.20		
<i>U</i>	0.098	1.7			0.94	2.9	0.42		
NIST ICPOES Mean				2.038					
<i>U</i>				0.018					
NIST PGAA Mean				1.980					
<i>U</i>				0.036					
ATI ICPOES Mean	5.58	95.9		1.980	30.2				
<i>U</i>	0.61	6.7		0.046	3.2				
ATI ICPMS Mean		93.1	9.42			182.6	19.4	7.73	
<i>U</i>		3.2	0.48			7.7	1.6	0.37	
Overall Mean	5.44	99.8	9.42	1.989	31.4	192.5	22.1	8.21	
<i>s</i>	0.20	6.3		0.034	1.7	9.3	2.7	0.69	
%rsd	3.7	6.3		1.7	5.5	4.8	12	8.3	

Table 5. Comparison of NIST ICPMS and WDXRF Results for SRM 1237

Method	Element:	P	Ti	V	Mn	Co	Ni
		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
WDXRF	Mean	21.6	< 20	15.2	12.2	6.13	12
ICPMS	Mean	85.7	13.50	20.32	6.50	5.03	20.17
	<i>U</i>	2.7	0.13	0.18	0.27	0.22	0.58
Certificate	Value	62	30	10	10	10	40
	<i>U</i>	-	-	-	-	-	-
		Cu	Nb	Hf	Ta	W	Mo
		(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
WDXRF	Mean	3.3	99.3	16.6	195.2	25.5	762
ICPMS	Mean	5.03	101.5	32.54	201.2	22.31	Not
	<i>U</i>	0.12	3.9	0.23	4.6	0.29	analyzed
Certificate	Value	10	85	31	200	25	< 10
	<i>U</i>	-	-	3	-	-	

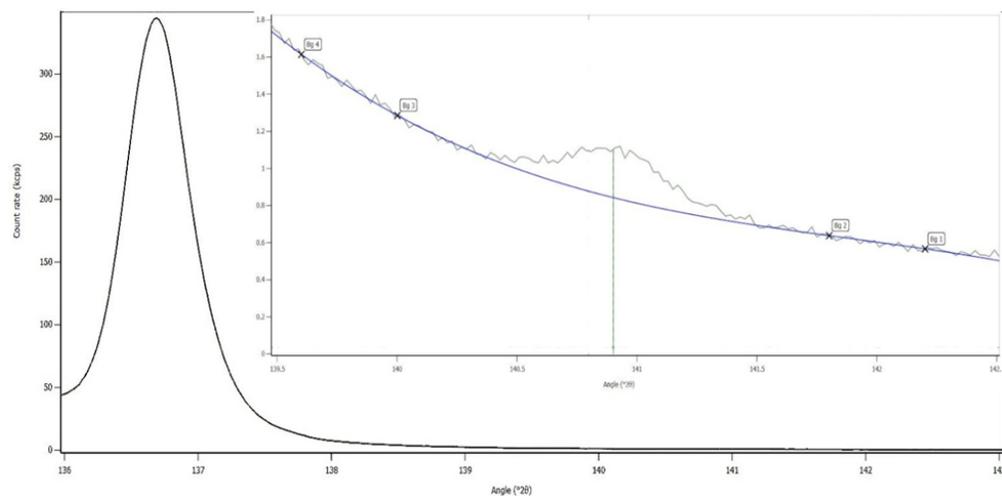


Figure 1. Scans of Zr and P lines using the laterally curved Ge(111) crystal. On the left, the large peak between 136 and 137.5 °2θ is the Zr L3-M4,5 peak from ≈ 6 % Zr in a bead of SRM 1215. The peak in the inset is the P K-L2,3 peak at ≈ 140.8 °2θ magnified ≈ 175x to make it visible. Four background locations and a fitted background model are shown with the enlarged P peak.

82x40mm (300 x 300 DPI)

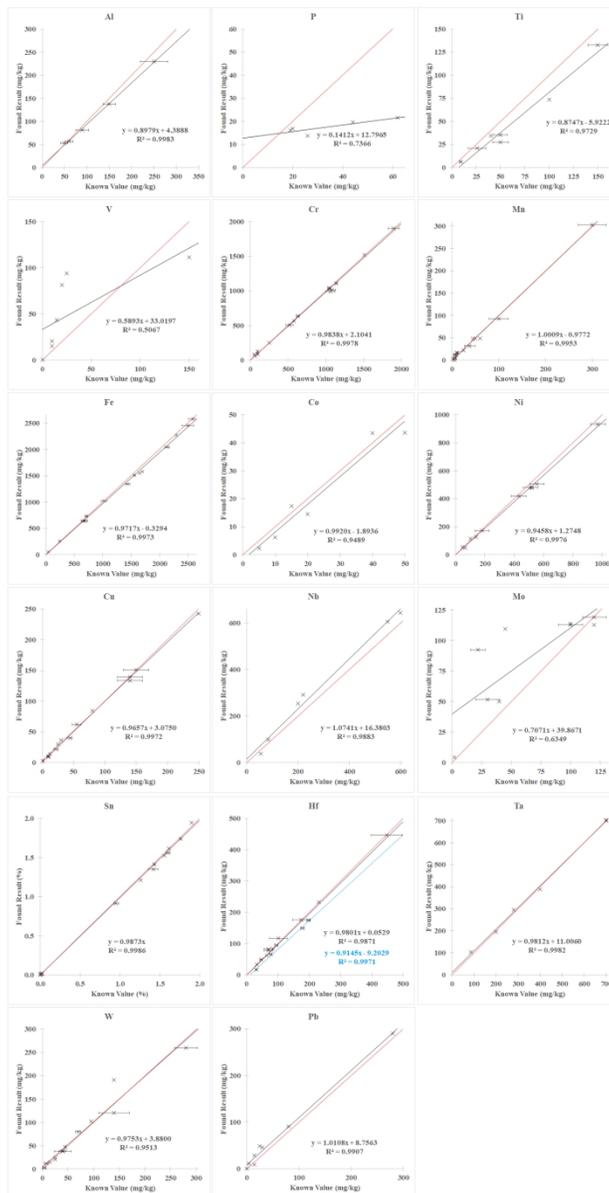


Figure 2. Correlations between found and known mass fractions for SRMs 360, 360a, 360b, 1210, 1211, 1212a, 1213, 1214, 1215, 1234, 1235, 1236, 1237, 1238, and 1239. Points with error bars are certified values and error bars show the approximate 95 % confidence interval. Other points are information values. The black line is fit to the data points. The red line is the ideal case where found and known values are identical. In the Hf graph, the blue line is fit only to the four SRM points that are closest to that line.

130x251mm (300 x 300 DPI)

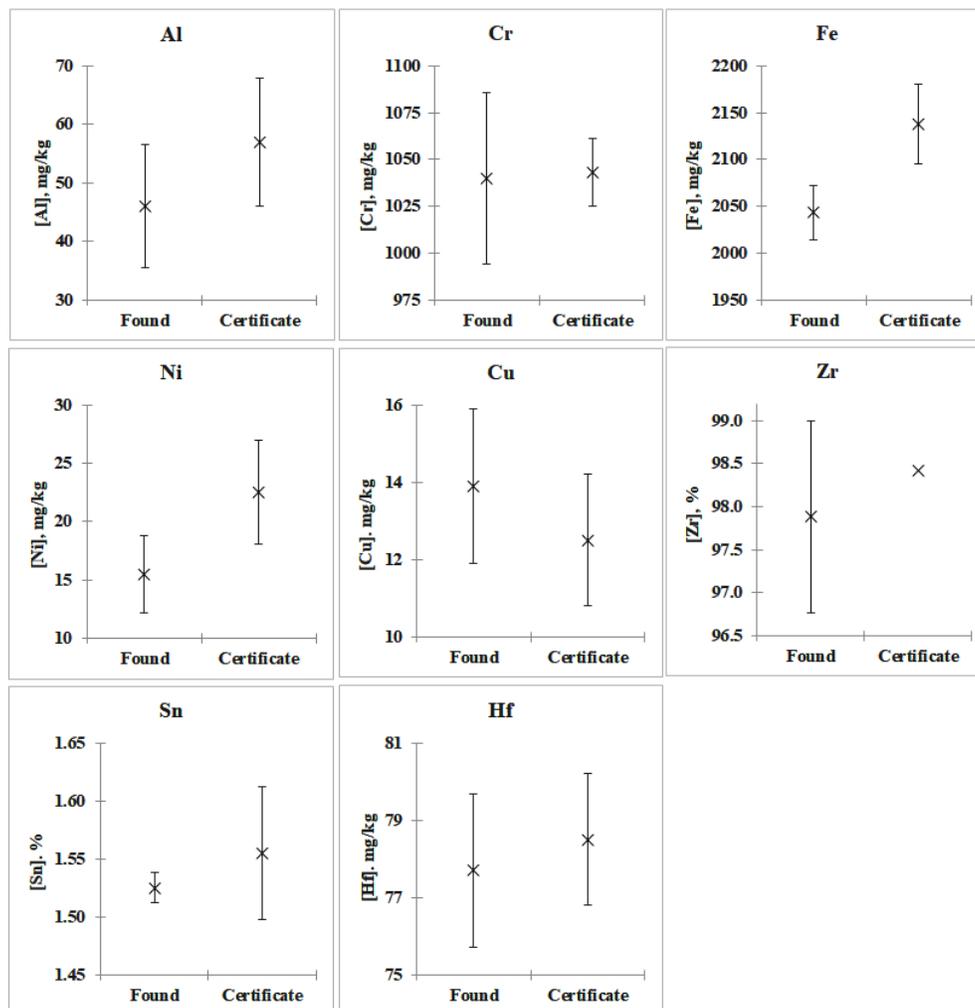


Figure 3. Graphical comparisons of found and certificate values in Table 3 for elements in SRM 360b analyzed as a quality assurance material. Error bars represent the 95 % coverage intervals, $U_k=2$, for the values. Certified values are for Cr, Cu, Fe, Hf, Ni, Sn. The value for Al is a reference value (non-certified), and the value for Zr is an information value.

69x71mm (300 x 300 DPI)